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Metallic behaviour of the electrochemically deposited Tl–Bi–Sr–Pb–Ca–Cu–O films down to 10 K

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Abstract : We have deposited, for the first time, $Tl_{1.5}$-$Pb_{0.5}$-$Bi_{0.5}$–Sr_2–Ca_2–Cu_2–O_x films on metal (silver) substrate by electrochemical method. The film is found to be non-superconducting down to 10 K. Electrical resistance of the films measured by four probe method indicates metallic character of the film down to 10 K. The X-ray powder diffraction patterns could be well fitted with tetragonal structure of the unit cell (with lattice constants a = 3.3858 Å and c = 29.8392 Å). The thickness of the films could be varied by changing the time of electrodeposition.

Keywords : Superconducting film, Tl–Bi–Pb–Sr–Ca–Cu–O, electrochemical deposition

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1. Introduction

Many attempts have so far been made to prepare high T_C superconducting films by various sophisticated techniques like sputtering [1], laser ablation [2], chemical vapour deposition [3] etc. All these techniques are quite sophisticated requiring costly instrumental facilities. It is also found difficult to deposit thin films on large surfaces by using the above mentioned techniques. Superconducting thin films on metal surfaces are suitable for applications in electronic transmission and energy storage using magnetic tapes. However, deposition of thin superconducting films on metal surface is, in general, inconvenient because of thermal expansion or lattice constant mismatch. For all these reasons development of electrochemical or similar other low cost and efficient techniques for the preparation of high T_C superconducting films are important. In our previous report [4,5], we have discussed the development of superconducting Bi–Sr–Ca–Cu–O films on Ag surface by a novel electrodeposition technique. Similar attempt has also been made in the present paper to deposite Tl containing superconducting oxide films. Here, we report on the behaviour of a typical electrochemically deposited Tl–Bi–Pb–Sr–Ca–Cu–O film (about 200 Å thick) on Ag substrate. Since we find it difficult to deposit Ba on the metal plate, our plan is to replace Ba by Bi and Sr in the Tl–Ba–Ca–Cu–O system and to investigate its superconducting behaviour (if any). The $Tl_{1.5}Bi_{0.5}Pb_{0.5}Ca_2Sr_2Cu_2O_x$ films studied are prepared by electrochemical method as discussed below.

2. Experimental

Highly pure (99.99 %) Bi_2O_3, $SrCO_3$, CuO, CaO, Tl_2O_3 and PbO oxides in appropriate proportion are dissolved in 20–25 % HNO_3 solution with pH value between 2 and 3. The solution was taken in a platinum beaker which acts as the anode and pure and highly polished silver plate or wire acts as the cathode on which thin film is deposited. A constant current source (Kiethley 220) is used to supply dc current (80–180 mA) between the electrodes. Uniform black film of Tl–Bi–Pb–Sr–Ca–Cu–O is deposited on the Ag plate which is immediately dried in vacuum and annealed at 780°C for a few minutes in flowing oxygen atmosphere.

3. Results and discussion

The X-ray diffraction patterns of the as grown unannealed and the oxygen annealed (at 780°C for 10 minutes) films are shown in Figure 1 and the scanning electron micrographs of the

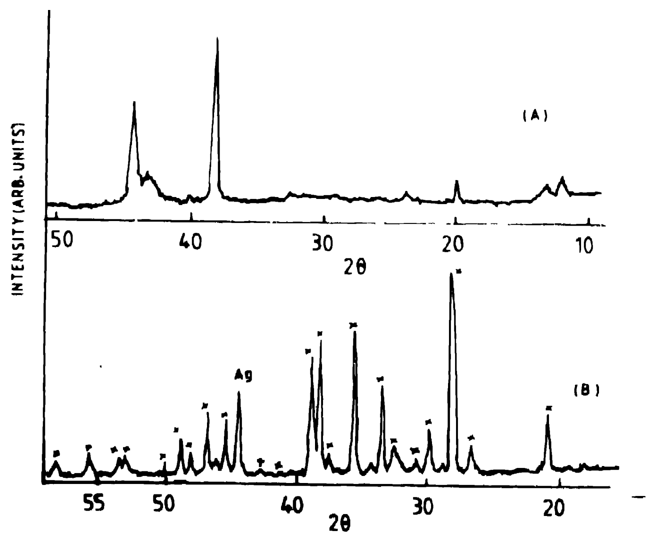
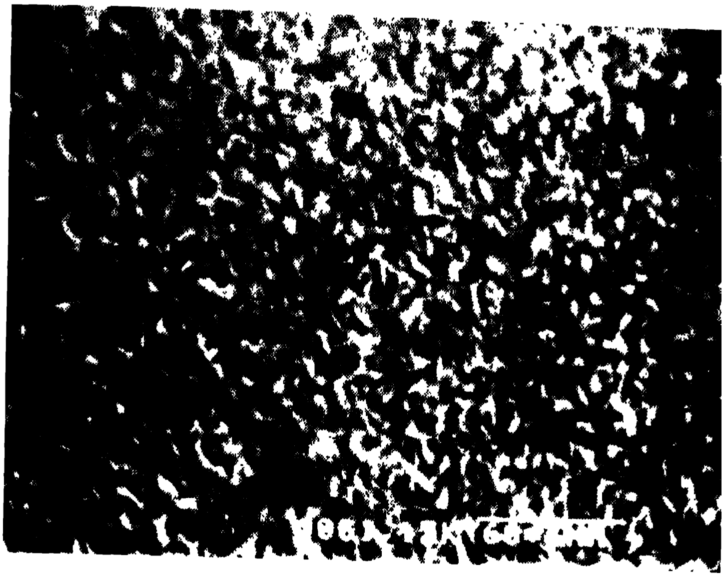


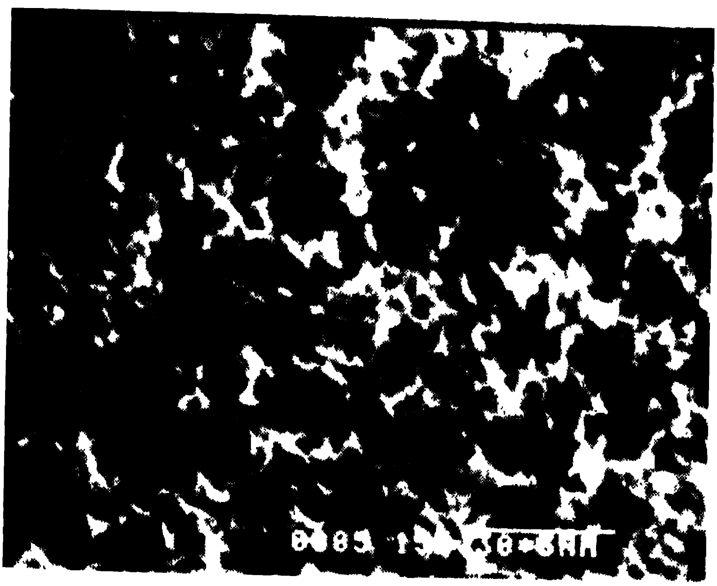
Figure 1. X-ray diffraction pattern of the as grown (unannealed) sample (A) and the final metallic sample after annealing at 780°C (B)

respective films are shown in Figure 2. The infrared spectra of the black unannealed powder collected from the films shown in Figure 3 indicates a band around 1350 cm^{-1} due to the presence of NO_x group in the film. This nitrous group is found to be not present in the final annealed sample. The X-ray patterns (star marked in Figure 1B) could be fitted with a tetragonal structure with lattice constants a = 3.3858 Å and c = 29.8392 Å.

Plate I



(A)



(b)

Figure 2. Scanning electron micrographs of the unannealed (A) and final annealed (B) films.

The electrical resistance of the film is measured by four probe technique similar to our earlier works [6] using closed cycle refrigerator unit (APD Cryogenics, USA). Temperature

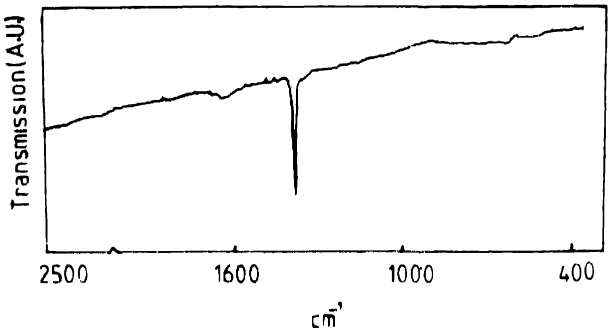


Figure 3. Infra-red spectra of the unannealed powder collected from the film.

down to 10 K was automatically controlled and measured by the unit. Thermal variation of electrical.resistance of the film is shown in Figure 4.

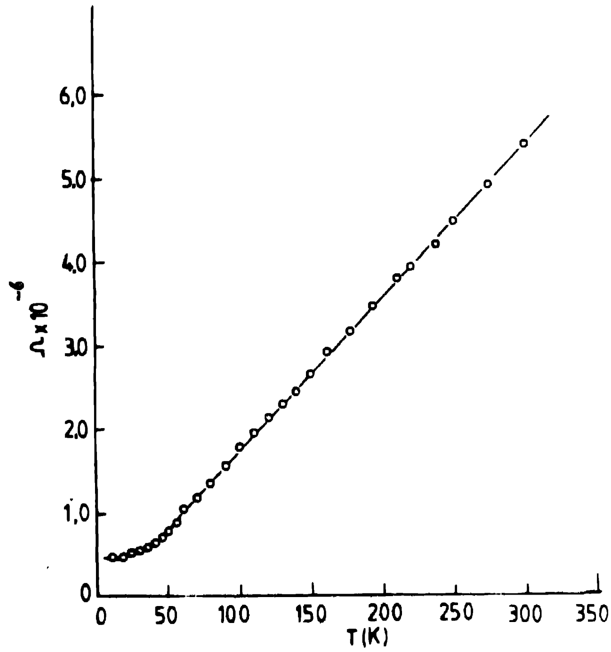


Figure 4. Electrical resistance of the final annealed film showing metallic character.

The metallic character of the film is indicated from the Figure 4. The film is not superconducting down to 10 K. However, improving the annealing technique under controlled oxygen pressure we have observed superconductivity in the Tl–Bi–Pb–Ca–Sr–Cu–O film around 50 K. This work is in progress in our laboratory and would be published elsewhere.

Acknowledgment

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